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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Inventor/Appellant: Partho Sarkar

Title: CRACK-RESISTANT ANODE-SUPPORTED FUEL CELL

Application No. 10/658,803

Filed: September 9, 2003

Examiner/Art Unit: ALEJANDRO, Raymond / 1745

Attorney File No.: 2281-001-03.

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APPEAL BRIEF

Dear Commissioner for Patents:

This is an appeal pursuant to 37 C.F.R. § 1.191(a) from the decision of the Examiner, dated June 5, 2006, finally rejecting claims 1-12 of the above-referenced patent application. A request for a one-month extension of time is enclosed pursuant to 37 C.F.R. 1.36(a).

Attached to this Brief as **Appendix A** is a claims appendix containing a copy of all the claims involved in the Appeal, as required under 37 C.F.R. §41.37(a)(viii). An evidence appendix as required under 37 C.F.R. §41.37(a)(ix) accompanies this Brief in the form of **Appendices B-E**. **Appendix B** contains pages from a publication that illustrates the oxygen ion conduction and high electrical conductivity characteristics of the solid electrolyte yttria stabilized zirconia ("YSZ") that make YSZ suitable for use in

the anode support layer of a solid oxide fuel cell ("SOFC"). **Appendix C** contains pages from a publication illustrating the relatively high electrical resistivity of alumina (aluminum oxide). **Appendix D** contains pages from a publication further discussing desirable characteristics of solid electrolytes suitable for use in SOFCs. **Appendix E** lists several Web sites that contain exemplary information illustrating the characterization and use of alumina as an insulator.

The objective evidence that accompanies this brief as **Appendices B-E** was made of record in the Response to final Office Action filed on October 11, 2006. This evidence was submitted after the final Office Action because this was when the Examiner first requested such evidence (See page of the Interview Summary mailed September 12, 2006). Thus, this evidence was necessary to fully respond to the Examiner's request and could not have been earlier presented since such a request had not been made until that point in the prosecution of the present application. These are certainly good and sufficient reasons pursuant to 37 C.F.R. § 1.116(e) and this evidence is therefore of record in the present application in accordance with 37 C.F.R. §41.37(c)(2).

A related proceedings appendix as required under 37 C.F.R. §41.37(c)(1)(ii) accompanies this brief as **Appendix F** and indicates there are no related appeals, interferences, or judicial proceedings, as is discussed in more detail in Section II below.

I. Real Party In Interest

The real party in interest is Alberta Research Council, Inc., having a principal place of business at 250 Karl Clark Road, Edmonton, Alberta T6N 1E4, Canada. The inventors assigned this application to Alberta Research Council, Inc. ("Assignee") in an Assignment recorded on February 9, 2004 at reel no. 014958, frame no. 0347.

II. Related Appeals and Interferences

Based on information obtained from Alberta Research Council, Inc., and based on information and belief of the undersigned attorney, there are no prior or pending

appeals, interferences, or judicial proceedings known to Appellant, Appellant's legal representative the undersigned attorney, or the Assignee, which are related to, which directly affect or which will be directly affected by, or which have a bearing on the decision of the Board of Patent Appeals and Interferences ("the Board") in the pending Appeal. There are no such appeals, interferences, or judicial proceedings as indicated in the related proceedings appendix that accompanies this brief as **Appendix F**.

III. Status of the Claims

Claims 1-13 are pending and stand rejected by the Examiner. Claims 1-12 are appealed.

IV. Status of Amendments

An Amendment After Final was filed on October 11, 2006 in response to a Final Office Action mailed on June 5, 2006. In an Advisory Action mailed on October 17, 2006, the Examiner indicated the proposed amendments in the Amendment After Final would not be entered as raising new issues that would require further consideration and/or search. **Appendix A** includes all the appealed claims 1-12 as they are currently pending.

V. Summary of the Invention

This summary of the invention provides cross-referencing to the application as required by 37 C.F.R. § 41.37(c)(v). This cross-referencing is solely to assist the Board in understanding the Applicant's invention and is not meant to be exhaustive or to limit the scope of the pending claims.

Independent claim 1 recites an anode-supported solid oxide fuel cell including an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. An electrolyte layer is in adjacent intimate contact with the anode support layer and a cathode layer is in adjacent intimate contact with the electrolyte layer. Figure 1 illustrates a planar anode-

supported solid oxide fuel cell 2 corresponding to one embodiment of invention covered by claim 1. The fuel cell 2 has a number of layers 10-18 in contiguous intimate contact, namely a cathode layer 10, an electrolyte layer 12, an anode functional layer (AFL) 14, an anode support layer 16 (ASL), and a pair of metallic current collectors 18 sandwiching these layers 10, 12, 14, 16. See paragraph 16. The current collectors 18 would typically be electrically coupled to an external circuit (not shown) to transmit electrons produced during the electrochemical reaction of the fuel cell 2.

As described in paragraph 18, the cathode layer 10 may be composed of magnesium doped lanthanum manganate (LaMnO_3) or a lanthanum strontium manganate (LSM), the electrolyte layer 12 made of a fully dense (*i.e.*, non-porous) yttria-stabilized zirconia (YSZ), which is an excellent conductor of negatively charged oxygen ions at high temperatures, and the anode functional layer 14 composed of porous nickel / zirconia cermet material. See paragraph 18. The ASL 16 is composed of a solid state YSZ structure impregnated with Ni or Ni-containing compounds. Other catalytic and electrically conductive materials may be substituted for the Ni or Ni-containing compounds. *Id.* The same is true of the YSZ structure, with other oxygen ion conducting materials suitable for SOFC use and having a relatively similar thermal coefficient to the electrolyte being substituted for YSZ. *Id.*

The ASL 16 is a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. The ASL 16 may be produced by sintering a powder containing YSZ and combustible additives at a temperature sufficient to enable the YSZ to achieve partial densification in a solid state and to burn out the combustible additives. Paragraph 19, line 7 *et seq.* The porosity is provided by way of interconnected pores formed as a result of the combustion of the sintering additives, with the target porosity of the ASL 16 being on the order of about 30% or greater. *Id.* After forming the porous YSZ ASL structure, the pores of the YSZ ASL structure are impregnated with nickel Ni or a nickel compound. This impregnation is then followed by heat treatment steps that are typically made in both oxidizing and reducing atmospheres, which causes the impregnated nickel to typically be in both metallic (Ni) and oxide (NiO) form. *Id.*

The impregnation process is carried out such that Ni/NiO is distributed thoroughly throughout the porous YSZ ASL structure in a sufficient quantity (below 75% of the pore volume, and typically below 50% of the pore volume) that, upon heat treatment, the Ni-phase is continuous through the inside of the YSZ ASL porous structure. See paragraph 20. This continuous distribution of Ni provides an electronic current path that enables the ASL 16 to serve as a current collector. After final heat treatment, Ni/NiO does not completely fill the pores in the YSZ ASL structure since the pores need to remain open to provide reactant gas passage through the ASL 16. *Id.*

As set forth in paragraph 21, during operation of the solid oxide fuel cell 2 fuel is supplied to and permeates through the ASL 16 and is oxidized to produce electrons. Under certain circumstances, such as when an insufficient amount of fuel is supplied for the electrochemical reaction ("fuel starvation"), the nickel Ni in the ASL 16 may oxidize to thereby form NiO. Paragraph 21, lines 2-4. Since NiO has a different density than Ni, its formation will cause a volume change relative to Ni. Paragraph 21, line 5 *et seq.* The Ni/NiO of the ASL 16 is, however, impregnated inside the porous YSZ ASL structure. *Id.* As a result, since the expected volume change associated with the oxidation of the Ni to NiO of the YSZ ASL structure is less than the volume of the pores in this structure, it is expected that no or minimal change in the overall volume of the ASL 16 will occur as a result of Ni oxidation. *Id.* The overall thermal expansion coefficient for the ASL 16 is also expected to be reduced as a result of using Ni-impregnated YSZ instead of a traditional zirconia-nickel cermet. *Id.*

In the ASL 16, the volume changes of this structure resulting from Ni/NiO oxidation and/or thermal expansion/contraction are expected to be less than in traditional cermet anode support layers. As a result, it is expected that the electrolyte layer 12 will experience less associated mechanical stress during operation, thereby reducing the occurrence of volume-change-induced cracking of the electrolyte layer. Although not discussed in detail, claim 1 also covers embodiments of the present invention illustrated in Figures 2-4.

Turning now to independent claim 12, this claim recites an anode-supported solid oxide fuel cell including a cathode layer in adjacent intimate contact with an

electrolyte layer that is in adjacent intimate contact with an anode functional layer. The anode functional layer is in adjacent intimate contact with an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, with at least some of the vias being filled with electronically conductive material. Claim 12 covers, for example, the embodiment of the present invention illustrated in Figure 2. In this embodiment, the ASL 16 is provided with a plurality of vias 20 (channels) that span the thickness of the ASL 16, and provide a pathway for the flowthrough of reactant gas. Paragraph 24, lines 2-3. The vias 20 may be created by one of the known methods in the art, e.g. by hole punching, *id.* at lines 3-4, and are filled with electronically conductive materials such as Ag, Ag/Ni -alloy or any other silver alloys, Cu or Cu alloys, Ni or Ni alloys, tungsten and its alloy, and so on, to enable the ASL 16 to serve as a current collector. *Id.* at lines 5-7. The rest of the ASL 16 structure may be substantially free of Ni or another electrically conductive material such that electric current flowing from the ASL 16 to the current collecting layer 18 flows mainly through the vias 20. *Id.* at lines 7-10. Alternatively, the rest of the ASL 16 structure may be impregnated with Ni/NiO to assist in catalyzing and current conduction. *Id.* at lines 10-11.

Figure 3 illustrates the ASL 16 having a graded composition along its thickness according to another embodiment of the present invention. Figure 4 illustrates another embodiment of the present invention in which a buffer layer 22 is introduced between the AFL 14 and the ASL 16.

VI. Issues

- 1. Whether U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. ("Shibata") anticipates claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e).**
- 2. Whether claims 7-8 and 10 are obvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al.**

("Sammes").

VII. Grouping of Claims

1. Claims 1-6, 9, 10, and 11-12 stand or fall together.
2. Claims 7 and 8 stand or fall together.

VIII. Argument

1. **Claims 1-6, 9, and 11-12 are allowable under 35 U.S.C. § 102(e) over U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. ("Shibata") because Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material.**

"Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim." *Gechter v. Davidson*, 42 USPQ2d 1030, 1032 (Fed. Cir. 1997). Before determining whether a prior art reference anticipates a claim, one must first construe the claim "to define the scope and meaning of each contested limitation." *Id.* The proper starting place in any claim construction analysis is the claim language itself read in view of the specification and the prosecution history. *Phillips v. AWH Corp.*, 415 F.3d 1303 (Fed. Cir. 2005) (*en banc*).

In the final Office Action mailed 5 June 2006, the Examiner maintained the rejections of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) as being anticipated by Shibata. On September 7, 2006, the undersigned along with the inventor Partho Sarkar and Brian Y. Lee, Canadian counsel for the Assignee, held a telephone interview with the Examiner to discuss the rejections of the pending claims (See the Examiner's Interview Summary mailed September 12, 2006 that is part of the file history of the present application). During this telephone interview, the Examiner construed the "porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material" recited in claim 1 as corresponding to the porous

métallic base body 1 illustrated in Figures 4-7. Paragraph 44 of Shibata states "it may be possible for the porous metallic base body [1] to be made of a ceramic which is plated with the above metals [e.g., nickel Ni] or with the alloy containing the above metals." Paragraph 69 more specifically provides "the porous base body 1 ... includes a ceramic (alumina) body plated with [nickel] Ni." In both the final Office Action (Item 2, bottom of page 3) and during the telephone interview, the Examiner erroneously concluded that the alumina portion of the base body 1 corresponds to the "porous ion-conducting structure" and the nickel Ni coating corresponds to the "catalytic and electronically conductive material" as recited in claim1.

Notwithstanding the Examiner's assertions, alumina is not a porous ion-conducting material. This fact is well understood and known by those skilled in the art. Alumina is an insulator having a resistivity that is too high for this material to be considered a solid electrolyte and an oxygen ion conductor suitable for use in a solid oxide fuel cell. In order for a material to be considered an oxygen ion conductor suitable for use in an electrode of a solid oxide fuel cell, the material must provide the necessary and efficient ionic path for anodic reaction which takes place during solid oxide fuel cell operation. As is well known in the solid oxide fuel cell art, the ionic conductivity of the anode must be comparable to the ionic conductivity of the electrolyte. Moreover, alumina's resistivity is too high at the operating temperature of a solid oxide fuel cell to perform the required electrode function for the fuel cell.

During the Examiner interview, the Examiner contended that even if alumina is considered in the prior art as an insulating material this material is nonetheless capable of conducting some ions, even if such ion conductivity is poor. See page 3 of the Interview Summary. The Examiner requested objective evidence to support that such an alumina ceramic is "incapable" of transporting ions, meaning that the material exhibits no ion conduction at all. *Id.*

A suitable material for the recited anode support layer and thus an ion-conducting material is yttria stabilized zirconia (YSZ). See, e.g., paragraph 8 of the present application. YSZ is an excellent conductor of negatively charged oxygen (oxide) ions at high temperatures. See paragraph 3. A solid oxide fuel cell operates at

an elevated temperature, typically on the order of between 700-1000 °C. *Id.* See page 101 of the Suresh publication that accompanies this amendment as **Appendix B** regarding general characteristics of ion-conducting materials. Other oxygen ion conducting materials suitable for use in a solid oxide fuel cell may be substituted for YSZ in the anode support layer. See paragraph 19. A characteristic of a solid electrolyte, which may otherwise be known as a fast ion conductor or a superionic solid, is a high electrical conductivity in the range of 10^{-1} - 10^{-4} ohm⁻¹cm⁻¹ (*i.e.* a resistivity of 10-10,000 ohm⁻¹cm⁻¹). See page 17 of **Appendix B**. In contrast, alumina (aluminum oxide) has a resistivity of 5.0×10^8 at 700°C and 2×10^6 at 1000°C (see page 959 of the Shackelford and Alexander publication, which accompanies this amendment as **Appendix C**. This large resistivity of alumina plainly evidences that alumina is not a solid electrolyte/fast ion conductor/superionic solid suitable for use in a solid oxide fuel cell. See the highlighted portions of the article that accompanies this amendment as **Appendix D** for additional information regarding desired resistivity values in fuel cells. **Appendix E** contains a listing of several Web sites that illustrate alumina being characterized and used as an insulator and not an ionic-conductor.

All the above evidence clearly demonstrates that the Examiner is in error in asserting that the alumina disclosed in Shibata corresponds to the recited porous ion-conducting material. Moreover, the Examiner's contention that because alumina must exhibit some ion conductivity the base body 1 of Shibata may be considered to correspond to the porous ion-conducting structure of the anode support layer recited in claim 1. Materials are classified as having physical characteristics that result in each material being placed in a particular class of materials, such as an electric or thermal conductor or insulator or an ionic conductor or insulator. Materials are not classified in absolute terms as would be required using the Examiner's logic. The Examiner requested evidence that "ceramic alumina is INCAPABLE of transporting ions (no ion conduction at all)." See page 3 of the Interview Summary. No such evidence can be provided for any material. Although classified as a particular type of material, every material will exhibit some characteristics of another class of materials. For example, materials classified as electrical insulators exhibit some amount of electrical conductivity, but such conductivity is so small that these materials are nonetheless

classified as insulators. If the Examiner's argument was accepted, then the classification of materials would be rendered meaningless. Any material could be said to be whatever type of material was needed by an Examiner when formulating a rejection.

Pursuant to MPEP § 2111, during patent examination the pending claims must be given their broadest reasonable interpretation consistent with the specification. The Examiner expressly mentioned this well known tenet of patent examination during the Examiner interview. As expressly set forth in Section 2111, the "broadest reasonable interpretation of the claims must also be consistent with the interpretation that those skilled in the art would reach." As evidenced by the accompanying technical literature, one skilled in the art would not interpret the phrase "ion-conducting structure" to include the insulating material of alumina ceramic. The Examiner's attempt to so interpret this phrase is simply put an unreasonable interpretation of this language. Although the Examiner cites the "broadest reasonable interpretation" language of Section 2111 as the rationale for his interpretation, such an interpretation of this language plainly in violation of this section of the MPEP as well as in contravention of common sense.

For all these reasons, Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material as recited in claim 1. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer. As discussed above, an alumina ceramic simply is not "a porous ion-conducting structure."

Because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. As previously discussed with reference to **Appendices B-E**, alumina's resistivity is too high for this material to be considered a solid electrolyte and an ion conductor for a solid oxide fuel cell. Alumina's resistivity is also too high at the operating temperatures of solid oxide fuel cells to carry out the required electrode function.

Furthermore, claim 1 recites an electrolyte layer in intimate contact with the anode support layer. Shibata discloses electrodes 10 and 11 to be in intimate contact with the electrolyte and not the base body 1 asserted by the Examiner to correspond to

the anode support layer. Thus, claim 1 is allowable for this additional reason.

For all these reasons, the combination of elements recited in claim 1 is allowable and dependent claims 2-11 are allowable for at least the same reasons as claim 1 and due to the additional limitations added by each of these claims.

Claim 12 recites an anode-supported solid oxide fuel cell comprising an anode support layer including an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure. At least some of the vias are filled with electronically conductive material. An anode functional layer is in adjacent intimate contact with the anode support layer and an electrolyte layer is in adjacent intimate contact with the anode functional layer. A cathode layer is in adjacent intimate contact with the electrolyte layer.

Shibata neither discloses nor suggests an anode support layer as recited in claim 12. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer since an alumina ceramic is not an oxygen ion-conducting structure. Simply because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. Alumina's resistivity is too high for this material to be considered a solid electrolyte and an oxygen ion conductor for a solid oxide fuel cell and the resistivity is also too high at the operating temperatures to carry out the required electrode function.

For all these reasons, the combination of elements recited in claim 12 is allowable.

During the interview, the Examiner also raised what he termed a potential 35 U.S.C. § 112, paragraph 1, issue regarding the recitation of an ion-conducting structure in the claims and pointed to paragraph 19 of the specification to support his assertion that only a description of oxygen ion conducting materials is contained in the application. See page 3 of the Interview Summary. The Examiner states that "the invention, as presently claimed, may have a [Section] 112 issue (lack of adequate written support, and may be [sic] lack of enablement) because it clearly does not disclose, suggest or teach how "ANY" ion conducting material can be suitably used in the claimed anode structure." While not at issue here a brief reply to this comment is

provided. It is the Examiner and not the Applicant that is inserting the word "any" before the claim term "ion-conducting structure" recited in claims 1 and 12. Claim terms must be construed in the context of the application. As expressly noted by the Examiner on page 3 of the Interview Summary, the present application (paragraph 19, lines 4-7) states "other oxygen ion conducting materials suitable for SOFC use and having a relatively similar thermal coefficient to the electrolyte, as is known in the art, may be substituted for YSZ." Claims 1 and 12 are directed to anode-supported solid oxide fuel cells. In the context of solid oxide fuel cells, one skilled in the art would understand the recited term "ion conducting structure" to relate to oxygen ions. No Section 112 issue exists.

2. Claims 7-8 and 10 are nonobvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al. ("Sammes") since there is no disclosure or suggestion.

In the final Office Action, the Examiner rejected claims 7, 8 and 10 under 35 U.S.C. § 103(a) as being obvious in view of Shibata and Sammes. As discussed above, nothing in Shibata discloses or suggests the recited anode support layer. Furthermore, Sammes describes anode layers that comprise different ratios of electrochemically active substance. Sammes also describes a process for manufacturing a solid oxide fuel cell anode wherein YSZ powder is added to NiO powder and these materials are milled, extruded, dried and sintered together. As discussed above, one would expect a cross-sectional micrograph of the base body described in Sammes to reveal a porous structure comprising a homogenous composition within each layer. There is no suggestion in Sammes to impregnate catalytic and electronically conductive material into the pores of an anode support layer, thereby creating an anode support layer having a non-homogeneous porous structure.

Claim 7 recites the fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other. The recited

porous structure is non-homogeneous in that the electronically conductive material of nickel Ni is compositionally graded through the thickness of the anode support layer. As a result, the anode support layer has a higher concentration of nickel Ni at one major surface than at the other major surface. Within the recited single anode support layer the electronically graded material is graded through the thickness of this single layer. Sammes discloses multiple layers with the concentration within each layer being homogeneous or constant and not graded. For these reasons, even if combined Shibata and Sammes do not teach or suggest the recited structure of claim 7. Claim 7 is accordingly allowable.

Claim 8 recites the fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material. Once again, Sammes neither discloses or suggest a single anode support layer having a nickel Ni concentration graded as recited in claim 7 and then a second conductive material concentrated at the major surface of the anode support layer having the lower concentration of nickel Ni as recited in claim 8. Claim 8 is accordingly allowable for these additional reasons.

3. Dependent Claims Not Specifically Addressed In Section VIII

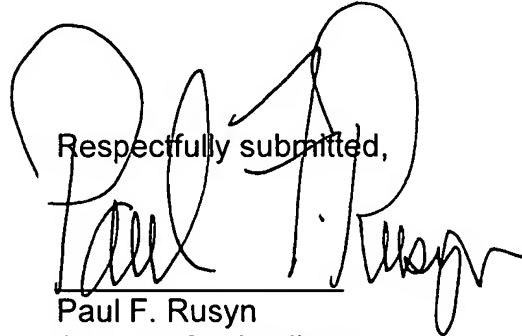
All dependent claims not specifically addressed in this section are patentable by virtue of their respective dependencies from claims for which the Applicants have presented an argument for patentability.

IX. Conclusion

For the foregoing reasons, the Applicants request the Board to reverse the Examiner's rejection of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) and his rejection of claims 7, 8, and 10 under 35 U.S.C. § 103(a) and remand the application to the Examiner for issuance of claims 1-12.

Enclosed is check number 27256 in the amount of \$620.00 to cover the fees associated with filing the Appeal Brief (\$500.00) and the extension of time fee (\$120.00).

Dated: February 8, 2007

Respectfully submitted,


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Enclosures:

Appendices A-F
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APPENDIX A

1. An anode-supported solid oxide fuel cell comprising
 - (a) an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material;
 - (b) an electrolyte layer in adjacent intimate contact with the anode support layer; and
 - (c) a cathode layer in adjacent intimate contact with the electrolyte layer.
2. The fuel cell of claim 1 wherein the catalytic and electronically conductive material is selected from the group of nickel, copper, silver, tungsten, and any alloys of these materials.
3. The fuel cell of claim 2 further comprising a second phase material mixed with the catalytic and electronically conductive material, the second phase material being selected from the group of yttria-stabilized zirconia (YSZ), doped cerium oxide, alumina or its salts.
4. The fuel cell of claim 2 further comprising an anode functional layer between the anode support layer and the electrolyte layer such that the electrolyte layer is in adjacent intimate contact with the anode functional layer instead of the anode support layer.
5. The fuel cell of claim 4 wherein the porous ion-conducting structure of the anode support layer is substantially yttria-stabilized zirconia (YSZ).

6. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is substantially evenly distributed throughout the anode support layer.
7. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other.
8. The fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material.
9. The fuel cell of claim 4 further comprising a porous zirconia-nickel cermet buffer layer sandwiched in between the anode support layer and anode functional layer, and having a porosity between 40-90%.
10. The fuel cell of claim 4 wherein the porous ion conducting structure of the anode support layer is comprised of a mixture of 10-30 vol. % of Ni, or NiO or both, and the balance yttria-stabilized zirconia (YSZ).
11. The fuel cell of claim 4 wherein the anode support layer further comprises a plurality of vias extending through the thickness of the ion conducting structure of the anode support layer, at least some of the vias being filled with an electronically conducting material.
12. An anode-supported solid oxide fuel cell comprising

- (a) an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, at least some of the vias being filled with electronically conductive material;
- (b) an anode functional layer in adjacent intimate contact with the anode support layer;
- (c) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
- (d) a cathode layer in adjacent intimate contact with the electrolyte layer.

13. An anode-supported solid oxide fuel cell comprising
- (a) an anode support layer;
 - (b) a porous cermet buffer layer in adjacent intimate contact with the anode support layer, and being composed of a zirconia-nickel cermet with a porosity between 40 and 90%;
 - (c) an anode functional layer in adjacent intimate contact with the buffer layer;
 - (d) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
 - (e) a cathode layer in adjacent intimate contact with the electrolyte layer.

*super-
ionic
solids*

PRINCIPLES
AND
APPLICATIONS

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CHAPTER 2

Superionic Materials and Structures

Superionic solids are ionic materials with high electrical conductivity comparable with those of liquid electrolytes. These materials are also termed "solid electrolytes" or "fast ion conductors". Typically a superionic solid has the following characteristics:

- (i) crystal bonding is ionic;
- (ii) electrical conductivity is high ($10^{-1} - 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$);
- (iii) principal charge carriers are ions which means that the ionic transference number (t_{ion}) is almost equal to 1 (here t_{ion} refers to the fractional contribution of the ionic conductivity to the total conductivity);
- (iv) the electronic conductivity is small; generally materials with electronic transference number (t_e) less than 10^{-4} are considered satisfactory superionic solids.

The values of electrical conductivity of a few ionic and superionic solids are shown in Figure 2.1. The highest conductivity at room temperature obtained so far is for RbAg_4I_5 which is $0.27 \text{ ohm}^{-1} \text{ cm}^{-1}$. This is many orders of magnitude higher than those of the more commonly known ionic solids KCl , NaCl etc. which have room temperature conductivity $\sim 10^{-12} - 10^{-16} \text{ ohm}^{-1} \text{ cm}^{-1}$. It may be noted that most of the superionic materials attain a high electrical conductivity above a certain temperature which may or may not be well defined. In other words, with increasing temperature the electrical conductivity sometimes changes gradually (as in β -alumina) or shows an abrupt jump (e.g. in β - AgI , RbAg_4I_5 etc.). Furthermore, for the latter materials the abrupt conductivity change is sometimes associated with a distinct structural change (like the $\beta \rightarrow \alpha$ transition in AgI) but sometimes this is not so clear (as in RbAg_4I_5). Structures which allow fast ion transport are generally disordered, "channelled" or "layered" (Wiedersich and Geller 1971). Ion-Ion interactions or correlation

over. Owens (1971) has noted that M^+ ions with volumes greater than $85(\text{\AA}^3)$ do not generally form conductive compounds. Furthermore, for bigger cations a lesser amount may be needed. For example, the maximum conductivity is obtained with 13 mole % MI for the $(\text{CH}_3)_4\text{NI}-\text{AgI}$ system, 12.5 mole % in the $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{NI}-\text{AgI}$ system and 12 mole % in the $(\text{C}_2\text{H}_5)_4\text{NI}-\text{AgI}$ system. This means that the percentage of added cations decreases with its increasing size as is expected from Raleigh's picture.

The above structural principles have been deduced on the basis of the very small amount of available structural data — mostly on cation substituted systems. More structural studies would be necessary both on anion and cation substituted systems to arrive at a better understanding.

2.8 Oxygen ion conductors

The first solid oxide electrolyte ever used was probably the ceramic with composition 85 wt % ZrO_2 , 15 wt % Y_2O_3 which was used by Nernst (1899) as an incandescent lighting material. Later Baur and Preis (1937) used this material for a fuel cell. The definite conductivity mechanism in terms of oxygen vacancies was proposed by Wagner (1943) and later verified by Hund (1952). However, the sudden increase of scientific interest in such materials started after Kiukola and Wagner (1957a, 1957b) illustrated their use in high-temperature thermodynamic measurements and fuel cells. In principle, almost all oxides can be expected to show some degree of oxygen ion conduction particularly the non-stoichiometric oxides. The non-stoichiometry can be created by heating the metal oxides in vacuum or oxygen or the relevant metallic vapour (Wagner 1974). Most of the oxygen ion conductors are good only at high temperatures ($\sim 1000^\circ\text{C}$) and are mixed conductors (ionic + electronic + electron-hole). As in the case of other ionic conductors, the conductivity in this case is strongly dependent on the temperature and doping with aliovalent impurities (like Ca^{2+} , Y^{3+} , Sr^{2+} etc. in HfO_2 , CeO_2 etc.) which control the number of point defects and their mobility. However, a unique property of oxide conductors is the dependence of the conductivity on the ambient pressure or activity. If the ambient oxygen pressure is low, the oxygen ions (O_O) would leave the solid electrolyte according to the following mechanism:

The defects are expressed in the Kröger-Vink notation: the symbol indicates the defect; the subscript the location of the defect; and the superscripts (') (.) denote negative and positive charges respectively. For example V_O'' means vacancy at the oxygen site having effectively two positive charges. Similarly, O_i'' would indicate an oxygen ion at the interstitial site with effectively two negative charges.

tions, cooperative hopping or correlation effects play important roles. Details of the conductivity mechanism will be discussed in Chapter 4. Figure 2.46 gives a schematic plot of conductivity as a function of partial pressure of ambient oxygen for a typical oxide electrolyte at three different temperatures: The higher the temperature, the lower is the range of oxygen pressure over which the conductivity is ionic. The dependence of the range of ionic conduction on concentration of aliovalent dopant (like Ca^{2+} or Y^{3+}) is shown in Figure 2.47. The effect of increasing concentration is to broaden the range of ionic conductivity and shift the whole conductivity curve to lower p_{O_2} values.

Most of the useful oxide electrolytes developed so far are based on ThO_2 , CeO_2 , HfO_2 and zirconia, though some other systems have also been described. For an earlier review see Etsell and Flengas (1970). The common structure which sustains high oxygen ion conduction is the "fluorite structure". The fluorite structure for MO_2 ($\text{M} = \text{metal ion Th, Ce etc}$) is shown in Figure 2.48. In this structure there are a large number of octahedral interstitial voids. Each metal cation is surrounded by eight

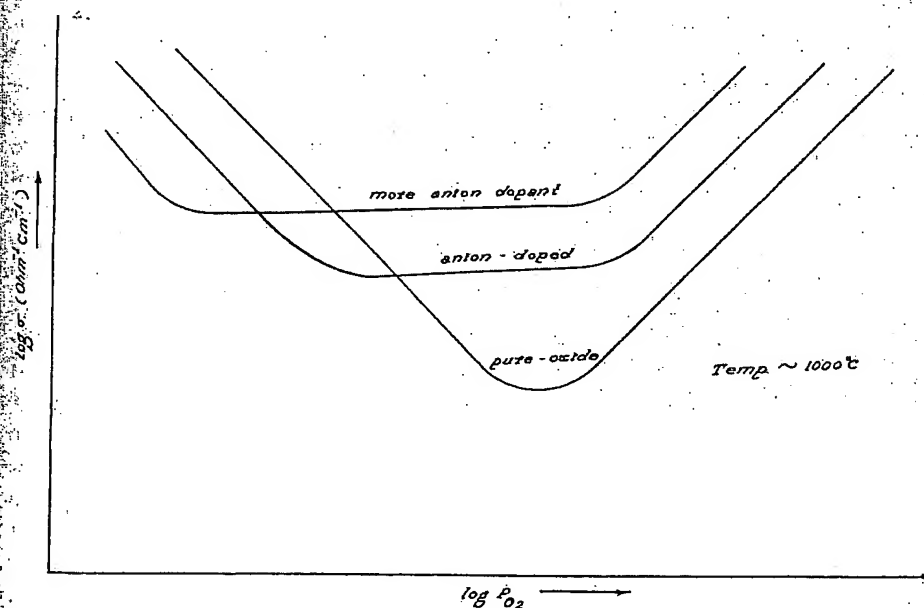


Fig. 2.47 Schematic representation of the dependence of conductivity of any oxide ion electrolyte on oxygen partial pressure for samples doped with different concentrations of aliovalent anion (Ca^{2+} , Y^{3+} etc.).

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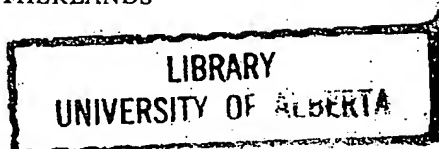
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**MATERIALS SCIENCE
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HANDBOOK**

THIRD EDITION

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and

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Table 291. RESISTIVITY OF CERAMICS

(SHEET 4 OF 6)

Class	Ceramic	Resistivity (Ω -cm)	Temperature Range of Validity
Oxides	Aluminum Oxide (Al_2O_3)	$>10 \times 10^{14}$	25°C
		2×10^{13}	100°C
		1×10^{13}	300°C
		6.3×10^{10}	500°C
		5.0×10^8	700°C
		2×10^6	1000°C
	Beryllium Oxide (BeO)	$>10^{17}$	25°C
		$>10^{15}$	300°C
		$1-5 \times 10^{15}$	500°C
		$1.5-2 \times 10^{15}$	700°C
		$4-7 \times 10^{15}$	1000°C
	Magnesium Oxide (MgO)	1.3×10^{15}	27°C
		$0.2-1 \times 10^8$	1000°C
		4×10^2	1727°C
	Silicon Dioxide (SiO_2)	10^{18}	room temp.
	Zirconium Oxide (ZrO_2) (stabilized)	2300	700°C
		77	1200°C
		9.4	1300°C
		1.6	1700°C
		0.59	2000°C
		0.37	2200°C

Source: data compiled by J.S. Park from No. 1 Materials Index, Peter T.B. Shaffer, Plenum Press, New York, (1964); Smithells Metals Reference Book, Eric A. Brandes, ed., in association with Rimer Research Institute Ltd. 6th ed. London, Butterworths, Boston, (1983); and Ceramic Source: American Ceramic Society (1986-1991).

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Materials for fuel-cell technologies

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Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. However, before fuel-cell technology can gain a significant share of the electrical power market, important issues have to be addressed. These issues include optimal choice of fuel, and the development of alternative materials in the fuel-cell stack. Present fuel-cell prototypes often use materials selected more than 25 years ago. Commercialization aspects, including cost and durability, have revealed inadequacies in some of these materials. Here we summarize recent progress in the search and development of innovative alternative materials.

The successful conversion of chemical energy into electrical energy in a fuel cell was first demonstrated¹ over 180 years ago. However, in spite of the attractive system efficiencies and environmental benefits associated with fuel-cell technology, it has proved difficult to develop the early scientific experiments into commercially viable industrial products. These problems have often been associated with the lack of appropriate materials or manufacturing routes that would enable the cost of electricity per kWh to compete with the existing technology, as outlined in a recent survey².

The types of fuel cells under active development are summarized in Fig. 1. The alkaline fuel cell (AFC), phosphoric-acid fuel cell (PAFC), proton-exchange membrane fuel cell (PEMFC) and solid-oxide fuel cell (SOFC) stacks essentially require relatively pure hydrogen to be supplied to the anode. Accordingly, the use of hydrocarbon or alcohol fuels requires an external fuel processor to be incorporated into the system. This then not only increases the complexity and cost of the system, but also decreases the overall efficiency as shown in Fig. 2. In contrast, molten-carbonate fuel cells (MCFCs) and solid-oxide fuel cells (SOFCs) operating at higher temperatures have the advantage that both CO and H₂ can be electrochemically oxidized at the anode. Moreover, the fuel processor can be accomplished within the stack, which enables innovative thermal integration/management features to provide excellent system efficiencies (> 50%).

Although the introduction of a 'hydrogen economy' might seem an attractive scenario, its implementation is beset with formidable technical and economic difficulties. The cheapest technology for the large-scale production of hydrogen is the steam reforming of natural gas, which produces significant emissions of greenhouse gases³. The topic of hydrogen storage is addressed in the accompanying review by Schlupbach and Zittel (see pages 353–358); indeed there is a breakthrough in the production of hydrogen and the development of new hydrogen-storage materials, the concept of a 'hydrogen economy' will remain an unlikely scenario. In this article, therefore, we assume that fuel cells have to be designed for operation on hydrocarbon or alcohol fuels to ensure that the technology is able to penetrate the relevant major markets. Otherwise fuel-cell technology will be confined to restricted niche activities where hydrogen might be a commercial option, such as city bus fleets. Clearly the choice of fuel is a

further complication in the factors influencing the commercialization of fuel cells.

Constraints on material selection

Materials selection for a commercial product involves an iterative design process that eventually becomes specific to the particular product and application. However, it is possible to make a few general statements about the selection of materials for fuel cells. The combined area-specific resistivity (ASR) of the cell components (electrolyte, anode and cathode) should be below 0.5 Ω cm² (and ideally approach 0.1 Ω cm²) to ensure high power densities with inputs of 1 kW dm⁻² and 1 kW kg⁻¹ are often mentioned for transport applications⁴. High power densities are also important to reduce costs, as the amount of material per kW is thus minimized. These topics, and considerations of cell efficiencies, are summarized in Box 1.

The need to minimize cell resistivities has a major impact on the selection and processing of the cell components. Cost-effective fabrication of porous electrode structures was achieved for the first time only about 40 years ago. The electrolyte, gaseous reactants, electrocatalyst and current collector have to be brought into close contact within a confined spatial region termed the triple-phase-boundary interface for the low-temperature systems, the introduction of hydrophobic polytetrafluoroethylene (PTFE or Teflon) greatly simplified the fabrication of porous, liquid-resistant gas-diffusion structures. Nickel or carbon powders (or porous carbon papers) provided the electronic pathways, and to further reduce the ASR of the electrode anode wire mesh or screen was usually incorporated into the structure. In the high-temperature systems, the performance was enhanced during the 1960s by the use of crystalline (ZrO₂) or amorphous (carbon powder or paper) electrolytes, Pt alloys, or on carbon powder or paper. In retrospect, this development was probably the first manifestation of an implemented nanotechnology, and it is not surprising that its implementation more than 40 years ago was so difficult.

High ionic conductivities (> 1 S cm⁻¹) associated with the liquid KOH, phosphoric acid and molten carbonate electrolytes ensured that, with appropriate design strategies, the ASR values of these components can be small. Although exhibiting lower specific ionic conductivity values, the Nafion membrane used in the PEMFC system can be fabricated relatively easily as a thick film (100 μm) to produce satisfactory ASR values, provided the water content of the film is controlled under the dynamic conditions of cell operation. In contrast, it has been, and continues to be,

Summary of Comments on Steele

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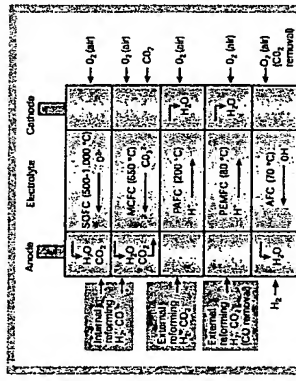


Figure 1. Summary of fuel-cell types. The oxidation reaction takes place at the anode (+) and involves the liberation of electrons. For example, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ or $\text{C}_2\text{H}_6 \rightarrow 2\text{CO} + 6\text{H}^+ + 6\text{e}^-$. These electrons travel toward the external circuit, producing electrical energy by means of the external load, and arrive at the cathode (-) to participate in the reduction reaction (for example, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ or $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$). It should be noted that as well as producing electrical energy and the reaction products (for example, H_2O and CO_2), the fuel-cell reactions also produce heat. The reaction products are formed at the anode (for SOFC, MCFC and AFC types) and the cathode (for PAFC and DMFC types). This difference has implications for the design of the entire fuel-cell system, including piping and heat exchangers. To maintain the temperature of the electrolyte component in the SOFC system, CO_2 has to be recirculated from the anode exhaust to the cathode feed. Additionally, the composition of the polymer-electrolyte electrolyte has to be carefully controlled during operation by an appropriate water management strategy.

difficult to scale-up thick-film technologies to provide cost-effective ceramic solid-oxide electrolyte components with required thicknesses in the range 10–30 μm . Usually the thick-film electrolyte has to be sintered at temperatures approaching 1,400 °C; this requires a porous ceramic substrate, which is often the anode or cathode material. The substrate material has to be carefully selected to avoid reaction with the electrolyte, and/or thermal expansion mismatch, during the high-temperature sintering process. The incorporation of a relatively weak, brittle structural component in SOFC stacks is at present restricting the application of SOFC systems to those situations that do not demand rapid temperature fluctuations. In this respect the recent development of sintering procedures below 1,000 °C, which should allow the use of metal substrates, represents a significant advance that will enable the development of more rugged SOFC systems.

Another important component in a fuel-cell stack is the impermeable electronic conducting bipolar plate. This has the dual function of distributing the fuel and air to the anode and cathode, respectively, as well providing the electrical contact between adjacent cells. The corrosive acidic conditions prevailing in the PEMFC and PAFC systems severely restrict the choice of bipolar plate material and at present graphite is usually selected. However, alternative materials or manufacturing methods are mandatory if these systems are ever to attain the target costs. Major research and development (R&D) programmes are underway to develop alternative carbon-based materials, such as carbon-fibre-reinforced polymers (CFRP). For the high-temperature systems (MCFCs and SOFCs) operating in the temperature range 500–750 °C, appropriate stainless steel compositions can be specified which seem to satisfy the technical and economic constraints. But for SOFCs operating at higher temperatures (800–1,000 °C), alternative, more expensive bipolar plate materials have to be specified, which at present incur significant cost penalties.

Additional constraints influencing material selection arise from reliability and durability issues. For transport applications, minimal values of performance degradation (for example, 0.1% over 1,000 h) are required for projected operational lifetimes of 3,000 h. But for stationary applications — for example, distributed CHP (combined heat and power) systems — similar degradation rate must extend over a period of at least 40,000 h (5 years). These different lifetimes impose very different demands on the materials and the engineering systems. The stack components were developed originally for transport applications.

A fuel-cell system incorporates relevant sub-components such as pumps, valves, heat exchangers and piping. Although these important components comprise at least half the cost of a fuel-cell system, we will not consider them further here, except to note that for the PAFC system, many of which have now been expanded for pebble-bed operation, 30,000 h, the main source of system breakdown has been balance-of-plant items. External fuel processors (reformers) are also the subject of intensive development around the world, and a variety of innovative compact reformers using diffusion-loaded printed-circuit components or micro-channel designs¹⁰ also illustrate the impact of materials technology on this aspect of fuel-cell systems.

For more than four decades now, reliable, efficient, fuel-cell systems incorporating AFC stacks have proved their worth in the Apollo spacecraft and space shuttles. Excellent electrode kinetics, when operating on pure hydrogen and oxygen, are an attractive feature of this system. But for terrestrial applications, the additional economic restraints, which include the need to replace hydrogen by cheaper hydrocarbon or alcohol fuels, have provided severe problems for materials selection and the associated fuel-processing technology. After 20 years development, the Elenco consortium abandoned attempts in 1986 to develop a bus powered by an AFC system. Although Zevco have purchased the technical rights, it is anticipated that market penetration of AFC systems will be small, in spite of a recent publication¹¹ advocating the use of AFC systems with ammonia as the source of hydrogen fuel.

Approximately 200 PAFC co-generation units (International Fuel Cells (IFC) PC25 systems, delivering 200 kW) have been installed around the world, and have exhibited excellent reliability. However, the commercial future of this system is possibly in jeopardy as the manufacturers (IFC and Japanese companies) have been unable to reduce the capital cost sufficiently below US\$3,000 per kW, as originally forecast¹². Most observers¹³ believe that for initial market entry the target cost per kW must be reduced to around US\$1,000 per kW, falling to below US\$500 per kW, with volume production. Accordingly, we focus here on materials aspects of the PEMFC, MCFC and SOFC systems, which at present still appear to present opportunities to exploit their potential.

It is important to note that the materials currently being used in PEMFC, MCFC and tubular SOFC prototype demonstration units essentially remain the same as those selected at least 25 years ago¹⁴. Although innovative fabrication and processing routes have improved the attributes (for example, lower cost and lower Pt loadings) of these materials, it is only in the past five years that system engineering and commercialization issues have highlighted the inadequacies of some of the materials originally selected. As indicated in the next two sections, it is these issues that are now driving the development of alternative materials, particularly for the PEMFC and intermediate temperature (IT)-SOFC stacks.

Polymeric-electrolyte-membrane fuel cells

The most important materials under development for PEMFC stacks are the proton-conducting electrolyte, the bipolar plates, electrode catalysts for the fuel and air electrode, and the ion-conducting membrane.

Depending on the fuel to be used in the PEM cell, the requirements for these materials are completely different. The simplest case is the operation with pure hydrogen and oxygen or air. Cells with high

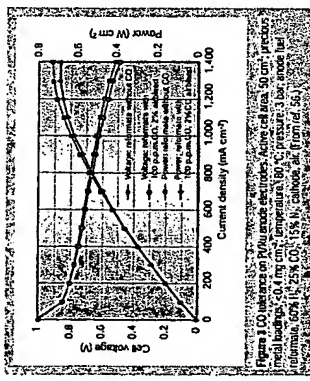


Figure 3 CO tolerance on PtRu anode electrodes. Anode cell area, 50 cm²; pressure, 1.5 bar; electrolyte, 0.5 M H₂SO₄; temperature, 80 °C; fuel, 1.5 bar; anode (PtRu), 0.5 M H₂SO₄; 1.5 bar; cathode, 0.5 M H₂SO₄; 1.5 bar (of 5.5).

support have been developed, and the reduction in noble-metal content without degrading the cell performance has been, and continues to be, an important R&D activity¹⁰. The platinum loading has been significantly reduced from 2 mg per square centimetre of electrode to values below 0.5 mg cm⁻² without significant impact on performance and lifetime. In the laboratory, even lower platinum loadings have been examined¹¹.

For fuels containing traces of CO, or methanol in the DMFC, a CO-tolerant catalyst is required. This remains one of the most challenging tasks for the successful development of commercial PEMFC systems¹². For reformate electrodes as well as for methanol oxidation, the removal of adsorbed CO species is the rate-determining step. The oxidation of adsorbed CO on Pt is slow, and is facilitated by adjacent adsorbed OH species. This is the reason why Ru, with its low potential for OH-ads formation, is the most efficient component of the binary catalysts. Pt/Ru and other binary and ternary alloys with these noble metals have been investigated intensively¹³, and performance values have increased significantly. The loss in performance is usually expressed in mV for a certain CO content of the fuel, and recent publications show promising results, as indicated, for example, in Fig. 3.

Membranes

Although the US General Electric Company (GE) initiated the development of PEMFCs in the 1950s. It was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially Nafion was manufactured¹⁴ for membrane cells used in the production of chlorine (chlor-alkali cells). By 1990, Ballard had overcome many of the engineering problems associated with PEMFC systems, and this had stimulated many groups in the United States and Japan to improve the properties of the original Nafion material¹⁵. For example, higher ionic conductivities could be obtained by selecting perfluorosulphonic acid copolymers with a short pendant group, and it was realized that gas and small-molecule permeability were other important characteristics that had to be improved.

The following properties of polymeric membranes need to be optimized for use in fuel cells: (1) high proton conductivity, assured by sulfonic groups (usually SO₃H), depending on sulfonation degree and on the membrane; (2) good mechanical, chemical and thermal stability; (3) low gas permeability; (4) low water uptake; (5) low methanol crossover; (6) low gas permeability; (7) low water uptake; (8) low methanol crossover. There is significant interaction between the desired properties of the membrane — high conductivity, low swelling, low gas and

methanol permeability, and stability — and the type of backbone polymer, the degree of sulfonation and the nano-phase separation into hydrophilic and hydrophobic domains (for example, high degrees of sulfonation usually lead to highly conductive membranes, but also to extreme swelling properties). To satisfy these requirements, different approaches have been examined: sulfonated perfluorinated materials with¹⁶ and without¹⁷ microporous support; sulfonated poly(ether)s; acid-base complexes and blends with a surplus of acid ionic groups; and inorganic-organic composite materials with improved thermal stability and better water-retaining properties¹⁸.

Both acid and PTFE-like backbones and relatively low equivalent weight. Nafion and related materials are a favoured option and are commonly used in fuel-cell stacks, but the costs remain high. Therefore much effort is being applied to develop alternative materials, usually fluorine-free, more cost-effective. But these options often suffer from an insufficient thermal stability, and more and more aromatic groups have been introduced into the polymer backbone. Polyarylene^{19,20} seem to be the most stable materials among the hydrocarbons. For example, poly(arylene ether sulphone) based membranes were prepared by sulfonation of easily available polymers such as Lule and Vitrac²¹. For high ionic conductivity, high sulfonation fractions are desirable, but high sulfonation can lead to extreme swelling even at room temperature. Thus, crosslinking of the polymer chains at the sulphonic acid groups can be included in the synthesis steps to overcome the problems of swelling. However, the long-term stability of these sulphonamide crosslinking bridges remains unproven. Alternative crosslinking methods such as covalent crosslinking and ionic crosslinking by the introduction of polymeric bases (acid-base blend membranes), have also been examined²².

For operation at elevated temperatures, which is desirable for high power density DMFC systems and for reformate fuels with CO levels above 100 p.p.m., the conduction mechanism becomes the dominant issue. In the types of membranes described earlier (hydroal-dominant polymers), the proton-conduction mechanism is based on the migration of hydrated protons. Above 100 °C, pressurized operation is required to ensure the presence of liquid water. Phosphoric acid and polymers with immobilized heterocycles exhibit a conduction mechanism relying on structure diffusion²³, and can be used at temperatures above the boiling point of water. As phosphoric acid in liquid form in a porous matrix is well known from PAFC development, new ways to achieve a composite with better properties have been investigated. One polymer material for high-temperature application is poly(benzimidazole) (PBI), which forms adducts with inorganic acids. Initial publications from Savinell²⁴ described the use of PBI with phosphoric acid as membrane in fuel-cell experiments. Later developments led to acid-base blend polymers with PBI and sulfonated poly(ether)etherketones. Reduced methanol permeability and performance data comparable to that of Nafion 112 have been reported^{25,26}. Advia (part of the Hoechst Celanese group) announced the manufacture of PBI-based membrane materials, but only in exclusive cooperation with partners (Plug Power and Ikon).

It should be emphasized that if an alternative membrane material does emerge, considerable R&D will still be necessary to optimize and manufacture the new membrane-electrode assembly (MEA). This development has taken many years for Nafion-type MEAs, although some of the expertise gained may be able to be transferred to the new system.

Fuel cells operating at elevated temperatures

In contrast to other fuel-cell types a SOFC stack can, in principle, be designed to operate within a wide temperature range (500–1,000 °C). It is necessary, therefore, to select the desired type of operation. This, in turn, is influenced by the specific application, the type of fuel and the properties of available solid electrolytes. For example,

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If the SOFC stack is to be integrated with a gas turbine, then system requirements indicate that the temperature of the exhaust gas from the stack should be about 1,500 °C. The steam reformer of the fuel gas, as well as the gas turbine, must be able to operate at temperatures in excess of 1,000 °C. But it is the properties of the solid electrolyte that exert the biggest influence on stack design and materials selection, as indicated earlier.

Figure 4 summarizes how the specific ionic conductivity of a selection of total electrolytes varies with the reduction of temperature. By taking a typical value of 0.15 Ω cm² for the maximum ASH value, it is possible to calculate the maximum thickness allowed for a given electrolyte component. For example, a design configuration that specified a self-supported (~150 μm) yttria-stabilized zirconia (YSZ) electrolyte would require a temperature of operation greater than 950 °C. Operation at 950 °C poses major problems for planar (flat) SOFC configurations compared to tubular configurations (see, for example, in the Siemens-Westinghouse arrangement). These include stability of the electrode-electrolyte interface, selection of the bipolar-plate material, and the optimal material composition and arrangement for the seals that are necessary in planar SOFC stacks. Extensive solutions are still sought today.

Owing to these intrinsic problems with the high-temperature planar configuration, there was early interest in tubular designs that eliminated the high-temperature sealing problems. A variety of tubular configurations was initially examined¹⁸, but the arrangement eventually adopted by Siemens-Westinghouse has so far proved the most successful. This arrangement uses a 1.5-m porous tubular cathode (La(Sr)MnO₃ or LSM). After deposition of the La(Sr)CO₃ interconnect strip by plasma spraying, an electrochemical vapor-deposition (EVD) process is used to fabricate an impermeable, thick-film (30–40 μm) electrolyte (YSZ) layer. The cell structure is completed by using a slurry-spraying process to deposit the porous Ni-YSZ anode. Although successful from a technical perspective, the EVD process is relatively expensive, and efforts are underway to replace this process by an alternative, cheaper fabrication route. However, conventional ceramic routes involving the deposition of YSZ powders and subsequent sintering are constrained by the need to restrict the sintering temperature to below about 1,250 °C to ensure

insufficient reaction between the LSM cathode and electrolyte. Selection of the cathode (LSM) and anode (Ni-YSZ) compositions was established during the 1970s by Westinghouse and ABB, after examining a variety of oxide compositions for long-term compatibility with YSZ at elevated temperatures. This compatibility was later explained in terms of avoided thermodynamic data¹⁹.

The Siemens-Westinghouse tubular design remains the most design of SOFC systems. It has been evaluated in units generating 25 kW, 100 kW, and 200 kW. More recently 200-kW units have been constructed with interconnectors to provide a system capable of generating electricity around 60% efficiency, large multi-megawatt long-run systems are in progress, and the technology is approaching 70%. However, the challenges remain concentrated with issues of system design rather than the selection and development of new materials.

Intermediate temperature solid-oxide fuel cells

The strategic programme of large multinational companies (such as Westinghouse, GE and ABB) focused the development of middle-temperature, high-temperature SOFC stacks and their interconnectors had a strong influence on the development of SOFC designs and materials for two decades from 1970. By 1990, however, it was beginning to be recognized that for smaller SOFC stacks not destined to be integrated with gas turbines, the operating temperatures should be lowered, as far as possible without compromising the electrode kinetics and internal resistance of the cell. The development of these smaller IT-SOFC stacks for distributed (embedded) CHP units, to produce stand-by power, is also being stimulated by liberalization (deregulation) of electrical supply policies. In addition, many automotive manufacturers are examining whether small SOFC stacks (3–5 kW) can be developed to supply the electrical power for auxiliary functions such as air conditioning in vehicles.

Examples of the most appropriate solid-electrolyte composition for operation at intermediate temperatures (500–750 °C) can be identified from Fig. 4. If we once again assume that the electrolyte component should not contribute more than 0.15 Ω cm² to the total cell ASR, then for a thick-film thickness (δ) of 15 μm, the associated specific ionic conductivity (σ) of the electrolyte should exceed 10⁻² S cm⁻¹ ($\sigma = I/ASR = 0.0015/0.15$). Examination of Fig. 4 indicates that the ionic conductivity of YSZ falls below this target value around 700 °C, and for Ce_{0.8}Gd_{0.2}O₃ (CGO) the relevant temperature is 500 °C. The use of thinner electrolyte films would allow the operating temperature to be lowered. But at present it seems that the minimum thickness for dense impermeable films that can be reliably mass produced using relatively cheap ceramic fabrication routes is around 10–15 μm. The use of a thick-film electrolyte requires this component to be supported on an appropriate substrate. As the substrate is the principal structural component in these cells, it is necessary to optimize the conflicting requirements of mechanical strength and gas-seal permeability.

AN IT-SOFC configuration that seeks to retain the specific advantages of both the tubular and planar arrangements is being developed by ABB-Allco²⁰. This integrated planar-stack concept incorporates multi-cell assemblies connected in series and supported by a ceramic substrate, and has many similar features to the original Westinghouse tubular design²¹.

The stack development work on planar IT-SOFC systems has involved thick-film YSZ electrolytes, and so far most groups have used anode (Ni-YSZ) substrates, which allow the electrolyte powder to be distributed on a dense film around 1,000 °C. One of the problems associated with using porous, composite Ni-YSZ substrates is their relatively poor thermal-expansion compatibility with the YSZ thick film. Accordingly, new groups are examining porous substrates based on Ni-Al₂O₃ or Ni-TiO₂ composites, with thin interfacial anode layers of porous Ni-YSZ and/or doped CeO₂. Although replacement of the YSZ can provide better thermal-expansion compatibility, problems still remain over the voltage changes expected

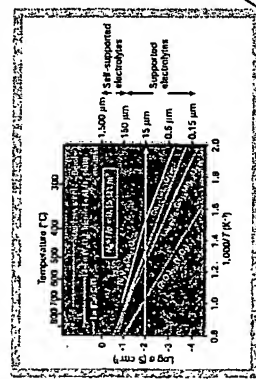


Figure 4 Specific ionic conductivity of various electrolyte materials. The curves represent the specific ionic conductivity of the electrolyte materials as a function of the inverse of temperature. The horizontal line indicates the specific ionic conductivity required for a 150 μm thick electrolyte layer to contribute no more than 0.15 Ω cm² to the total cell ASR. The materials shown are: YSZ (yttria-stabilized zirconia), CGO (Ce_{0.8}Gd_{0.2}O₃), and others. The conductivity of YSZ drops below the required value around 700 °C, while CGO remains above it down to 500 °C.

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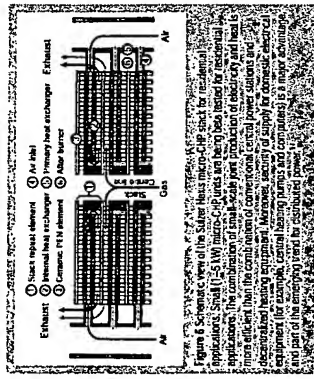
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with the reduction and oxidation of the Ni component. As the porous substrate-electrolyte film is usually coated in air, nickel is oxidized to NiO, which has a low thermal expansion coefficient. During the initial heating cycle of the fuel cell, the NiO is reduced to Ni, which has a higher thermal expansion coefficient. Additionally, operating procedures have to be developed to prevent the nickel-oxidizing when SOFC stacks are cooled down in the absence of fuel flowing through the anode compartment (of note here is the use of forming gas, N_2/H_2 , to protect the Ni-YSZ anode in the Siemens-Westinghouse tubular configuration).

Most IT-SOFC developers are using metallic bipolar plates. Often a ferritic stainless steel is specified because of the low ($12.5 \times 10^{-6} K^{-1}$) thermal-expansion coefficients of these alloys. Moreover, by using compositions stabilized with Ni-Ti, excellent electronic interfacial contacts can be maintained between the cell components for extended periods. Providing appropriate precautions are followed, many R&D laboratories have reported good performance values for IT-SOFC stacks incorporating the following positive-electrolyte-negative (PEN) components: anode-supported thick-film YSZ electrolytes, LSM-YSZ cathodes, and stainless steel bipolar plates.

To minimize sealing requirements, many IT-SOFC stacks have adopted a circular design in which the fuel and air are introduced by means of an appropriate manifold at the centre of the PEN structure. Arrangements are made to distribute the air and fuel gases over the cathode and anode, and the flow rates are adjusted to ensure almost complete conversion of the fuel by the time it reaches the stack periphery. Unreacted fuel and air are then combusted without large temperature changes. These design features minimize sealing problems and allow limited thermal cycling. Examples are provided by the Silver Hacks Interim-Cell (IHIC) configuration designed for residential accommodation (Fig. 5), and the auxiliary power unit (APU) prototype (Fig. 6) constructed by the Döhring-IMW-Gabai Thermoelectric consortium for incorporation into vehicles. But at present the heating and cooling rates cannot exceed $\sim 500^\circ C$ per hour, owing to the development of stresses associated with thermal-expansion mismatch, and to the brittle glass and ceramic seals. Although this restriction may not be too severe for larger CIP systems ($>100 kW$), it is not satisfactory for smaller systems (1–10 kW) designed for micro-CHP and APU applications. Further R&D is still required to produce more rugged IT-SOFC stacks. Commercial units can be expected in the next five years once reliability and cost requirements ($<US\$1,000$ per kW) have been effectively demonstrated.

IT-SOFC stacks incorporating alternative components. Although YSZ is still the favoured electrolyte material for SOFC stacks, selection of this material is not without problems and research

continues into the long-term evaluation of samaria-doped ZrO_2 , which can exhibit higher ionic conductivities than the traditional YSZ material.

In principle, the use of ceria-based electrolytes such as CGO should allow the cell operating temperature to be lowered to around $500^\circ C$ (see Fig. 4). But perceived problems associated with PEN structures incorporating ceria-based electrolytes have restricted investment in this technology. It is well known that, at elevated temperatures, Ca^{2+} ions can be reduced to Ca^0 under the fuel-rich conditions prevailing in the anode compartment. The associated electronic conductivity (and deleterious fuel expansion) produces an internal short circuit in the PEN structure, which can significantly degrade the efficiency and performance of the cell. However, if the operating temperature is lowered to around $500^\circ C$, then the electronic conductivity is small, and can be neglected under typical operating conditions of the cell.

Another significant difficulty that has restricted exploitation of the attractive properties of CGO at $500^\circ C$ has been the need to develop alternative ceramic compositions that function effectively at lower temperatures. Recent developments in this area have been surveyed by Raj et al.¹¹ and there are indications that appropriate materials for composite cathodes can be fabricated which exhibit mixed 600-potential at $500^\circ C$ (for example, $0.15 V$ at $1 A cm^{-2}$). Composite anodes such as Ni-CGO also provide adequate performance at $500^\circ C$ for simulated syngas fuels, indicating that IT-SOFC operation at this temperature is viable.

Operation at low temperatures, however, requires initiating R&D effort into alternative anodes. One strategy is to develop the anode using oxides that are redox stable, to avoid the use of Ni. This needs an anode carbon deposition under certain operating conditions, and also forms NiO, which is accompanied by a deleterious volume expansion, when the anode compartment becomes too oxidizing. Another approach is concerned with the identification of alternative anodes that allow the direct anodic oxidation of hydrocarbons. The claims made in recent publications^{12,13} remain controversial¹⁴, but there is little doubt that this topic will remain a fruitful area for further investigations.

Operation at $500^\circ C$ allows the use of compliant high-temperature gaskets in place of rigid, brittle glass or ceramic seals, thus permitting greater design flexibility for the stack configuration. At Imperial College, London, researchers have taken advantage of the fact that the thermal-expansion coefficient of CGO and ferritic stainless steel are virtually identical ($12.5 \times 10^{-6} K^{-1}$), so that the thick-film PEN structure can be supported on a porous stainless steel foil. These metal-supported PEN structures are robust, and should withstand the rapid temperature cycles expected during operation of small IT-SOFC stacks.

Another electrolyte, doped $LaGaO_3$ (LSGM), is also attracting much attention for IT-SOFC applications. Although its conductivity is slightly smaller (see Fig. 4) than CGO at $500^\circ C$, its ionic domain is wider and it could be more appropriate to use this electrolyte at temperatures around $600^\circ C$, where the reduction of Ce^{4+} in CGO becomes significant. It has been difficult to fabricate pure single-phase ceramic electrolytes, and second phases such as $SrLaGaO_3$ and $LaGaO_3$ are often detected in the grain boundaries. Whether these phases are responsible for the enhanced reactivity of LSGM, or whether it is an intrinsic property of LSGM, are questions that require urgent research. Moreover, the preferred composition, $La_{0.9}Sr_{0.1}Ga_{0.9}O_{3-\delta}$, does not seem to be stable at lower temperatures ($<600^\circ C$). Although research continues into the synthesis of alternative oxygen-ion conducting electrolytes, it has proved difficult to prepare alternative materials with an appropriate combination of properties that can displace the traditional fluorite compositions involving ZrO_2 and CaO .

Experiments involving single-component SOFC fuel cells have been reported. In this configuration a mixture of the fuel and air flows

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over both electrodes of a ceramic cell. One electrode incorporates an electrocatalyst optimized for the reduction of oxygen, whereas the second electrode is designed to catalyze the fuel oxidation. This configuration eliminates the need for cell sealing and excellent current-voltage (I - V) characteristics have been reported¹⁰. But the published data need to be interpreted with caution as it seems that the electrodes also catalyze the external oxidation of the fuel. The heat generated by these surface reactions can significantly raise the temperature of small samples, so that the reported data probably refer to I - V values around 100 °C higher than those stated. Parasitic chemical oxidation of the fuel will of course significantly reduce the overall system efficiency, and technological exploitation of this configuration seems unlikely.

Very high performance have been claimed¹¹ at 500 °C using composite electrolytes incorporating CGO and molten salts. But the long-term stability of such mixtures in a fuel-cell environment must be doubtful and these claims require further independent scrutiny. Investigations also continue into ceramic proton conductors. The composition $Ba_{0.9}La_{0.1}O_{3-x}$, for example, can exhibit a protonic conductivity that approaches that of the oxygen-ion conductivity of CGO at 500 °C (that is, 10^{-2} S cm⁻¹). But solid-state fuel cells incorporating such proton conductors will not be able to electrochemically oxidize CO and do not, at present, appear to offer any advantages over the existing molten electrolyte technology for this temperature region. Interesting results have also been reported¹² for the solid acid CH_3SO_3H at 160 °C. Ceramic protonic conductors are more likely to be exploited in chemical engineering applications requiring the separation and generation of hydrogen.

Molten-carbonate fuel cells

Although the materials (Table 1) used for MCFC stack components have essentially remained unchanged¹³ over the past 25 years, significant developments in fabrication technology were introduced during the 1980s. Cost-effective tape-casting techniques now allow the immobilized electrolyte matrix to be manufactured up to a size of 1 m². These manufacturing advances were important as the power

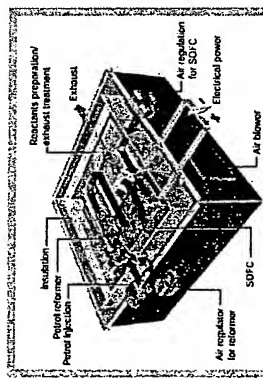


Figure 1 Schematic view of the top-down (left) and side (right) views of a Molten-Carbonate Fuel Cell (MCFC) stack. The stack is composed of a series of cells, each containing a molten carbonate electrolyte. The stack is housed within a stack housing. The reformate and pre-reform gases enter from the left, and the exhaust gases exit from the right. The air and air reformer gases enter from the right, and the electrical power is generated from the stack.

density of MCFC systems operating at 650 °C is relatively low (~ 150 mW cm⁻²), requiring large cell areas to be fabricated. The requirement to recirculate CO₂ from the anode exhaust to the cathode to maintain the composition of the carbonate electrolyte also complicates the balance-of-plant equipment. It follows that the MCFC is only likely to be commercialized only at sites greater than 100 kW, and originally MCFC plants were conceived as large (multi-megawatt-scale), centralized coal-fired power stations.

To develop user confidence it was considered that large plants should be demonstrated as soon as possible, and this led to the construction in the United States of the 1.8-MW Santa Clara system by Energy Research Corporation. Although commissioned in April 1986, evaluation of the plant had to be curtailed owing to problems with the material selected for the stack external manifold. It is now believed that more appropriate strategy is to develop smaller MCFC systems (~ 250 kW) for distributed CHP applications using natural gas. An example of this approach is provided by the 300-kW 'Hot Spot' unit, developed by MTU Friedrichshafen (a subsidiary of DaimlerChrysler AG), and it is encouraging to note that the first demonstration run (8,000 h) of an electrical efficiency of 40% because of the cost of the molten salt LiAlH₄CO₃ electrolyte. However, a recent appraisal¹⁴ suggests that most commercial plants should attain the target value of 40,000 h, except possibly the coatings used to protect the anode structure, which remains the focus of further materials development.

Operating procedures for MCFC systems are influenced by limitations associated with two of the components. In cooling down the hot stack in the absence of a fuel supply, it is necessary to protect the Ni-Cr anode from oxidation by the introduction of an inert gas into the anode compartment. More serious, however, is the inability of the immobilized electrolyte matrix to withstand more than 3 to 5 thermal cycles through the melting point of the molten salt electrolyte. Thus, during stand-by situations the temperature of the MCFC stack must be maintained high enough to prevent solidification of the molten salt electrolyte. Clearly both the MCFC and SOFC markets will initially be competing for the same sub-megawatt CHP market sector. It is expected that both will operate at similar electrical efficiencies, and so the cost of the installed plant will determine which technology eventually has the largest market penetration. It is also interesting to note that both fuel-cell types require procedures to prevent redox reactions damaging the anode, and to restrict thermal cycling of the plant during abnormal operating situations.

Conclusions

Probable applications of fuel cells in the next decade together with a selection of critical materials issues are summarized in Table 2. It is recognized that the capital costs ($\$33,000$ – $10,000$ per kW) of prototype fuel-cell systems are too high. Although volume production can be expected to reduce these costs, it may be difficult to attain sufficient market share to justify the investment for mass production while competing against established technology. Although significant niche markets exist, such as the PEMFC system for city buses, many observers believe that a more appropriate strategy is to target those sectors of the market (for example, 1–10 kW generation) where the existing technology is inefficient and displays extremely poor

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